

Performance of the TPSS Functional on Predicting Core Level Binding Energies of Main Group Elements Containing Molecules: A Good Choice for Molecules Adsorbed on Metal Surfaces

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Abstract

Here we explored the performance of Hartree-Fock (*HF*), Perdew-Burke-Ernzerhof (*PBE*), and Tao-Perdew-Staroverov-Scuseria (*TPSS*) functionals in predicting core level 1s Binding Energies (*BEs*) and BE shifts (ΔBEs) for a large set of 68 molecules containing a wide variety of functional groups for main group elements B \rightarrow F and considering up to 185 core levels. A statistical analysis comparing with X-Ray Photoelectron Spectroscopy (*XPS*) experiments shows that *BEs* estimations are very accurate, *TPSS* exhibiting the best performance. Considering ΔBEs , the three methods yield very similar and excellent results, with mean absolute deviations of ~ 0.25 eV. When considering relativistic effects, *BEs* deviations drop approaching experimental values. So, the largest mean percentage deviation is of 0.25% only. Linear trends among experimental and estimated values have been found, gaining offsets with respect ideality. By adding relativistic effects to offsets, *HF* and *TPSS* methods underestimate experimental values by solely 0.11 and 0.05 eV, respectively, well within *XPS* chemical precision. *TPSS* is posed as an excellent choice for the characterization, by *XPS*, of molecules on metal solid substrates, given its suitability in describing metal substrates bonds *and* atomic and/or molecular orbitals.

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1. Introduction

X-ray Photoelectron Spectroscopy (*XPS*), also known as Electron Spectroscopy for Chemical Analysis (*ESCA*), is an experimental technique available in many materials and surface science laboratories and facilities and is essentially used for the chemical or elemental analysis of bulk materials, but especially for surfaces because of its surface sensitivity.^{1,2} In addition, XPS is a technique currently used to observe *in situ* the evolution of an heterogeneously catalyzed reaction, allowing for the characterization of reactants, intermediates, and products, thus serving as a powerful tool to determine the reaction mechanism.³⁻⁵

The XPS performance on elemental analysis hangs on the measurements of core level electron Binding Energies (*BEs*). The *BEs* are characteristic of a given element and, more importantly, of a given element in a given chemical environment and electronic state. Thus, *BEs* provide quantitative information of the chemical composition and also on the physicochemical properties including insights of the electronic structure, thus providing more significant information apart from those obtained by the elemental analyses.¹⁻⁵ *BEs* from XPS experiments in condensed phase systems provide chemical fingerprints but also reflect the chemical properties and bonding between the species in a given system.⁶ The small variations for a type of atom in different chemical environments are often referred to as *BEs* shifts (ΔBEs) and provide meaningful information. This is used to distinguish structural as well as oxidation state of the atom.⁷

Core level *BEs* and their respective shifts can be accurately predicted from *ab initio* calculations at the well-known Hartree-Fock (*HF*) theory⁸⁻¹⁰ to currently used Density Functional Theory (*DFT*) based methods,¹¹⁻¹³ especially with hybrid functionals

as recently illustrated for N-containing molecules in gas phase.^{14,15} Nevertheless, one must admit that prediction of BEs and especially of Δ BEs will be especially relevant and highly desirable for molecules adsorbed on metal surfaces. In fact, transition metal (*TM*) surfaces are ubiquitous in heterogeneous catalysis as supported active phases, but also employed in chemical resolution, nanotechnology, synthesis, and other related processes of technological interest.

Unfortunately, hybrid functionals are not especially well suited for metals^{16,17} because of the failure to attain the exact homogeneous electron gas limit.¹⁸ In fact, recent studies¹⁹⁻²¹ show that, among various *DFT* methods including Generalized Gradient Approximation (*GGA*) type, meta-*GGA* and hybrid density functionals, the *GGA*-type Perdew-Burke-Ernzerhof (*PBE*)²² implementation of the exchange-correlation potential provides the best description of the structural, energetic, physical, and electronic properties for all *3d*, *4d*, and *5d* TMs. On the other hand, hybrid functionals²³ are required for a good description of the thermochemistry of main group elements.²⁴ In heterogeneous catalysis one has simultaneously to describe main group element molecules and transition metal surfaces which leads to a dilemma regarding the appropriate choice of the *DFT* method, *GGA* type functionals being usually selected.²⁵ Here it is worth to mention that recently it has been shown that the meta-*GGA* type Tao-Perdew-Staroverov-Scuseria (*TPSS*)²⁶ functional provides a description of the three transition metal series nearly as accurate as *PBE*.¹⁹ Note also that compared to *PBE* and other *GGA* functionals, being a meta-*GGA*, *TPSS* represents an improvement in describing the thermochemistry of main group molecules. In this sense, *TPSS* seems to be a good choice to describe the interaction of molecules with transition metal surfaces.

In the present work we assess the performance *TPSS* in providing estimates of BEs and Δ BEs for a wide variety of molecules including the main group heteroatoms

(B→F) and encompassing possible chemical interactions by selecting a vast dataset, with the eye put on subsequent studies aimed at describing similar molecules in contact to metal surfaces. For comparison, HF and PBE are also used since HF is a standard method in molecular quantum chemistry and PBE is a prototypal functional used in theoretical heterogeneous catalysis and surface science.²⁵

2. Core Level Binding Energy Theory Background

Core level BEs can be rather accurately predicted from *ab initio* calculations, such as HF or DFT based methods.⁸⁻¹⁵ Absolute BEs are obtained from the difference between the total energies of the neutral state and the same system with a core hole configuration generated by subtracting one electron in the desired core level as in Eq. 1.

$$BE = E(\text{Core hole state}) - E(\text{Neutral state}) \quad (1).$$

A possible way to obtain the energy values in Eq. 1 is to make use of separate Self-Consistent-Field (*SCF*) calculations. The resulting procedure usually referred to as Δ SCF approach^{8,10} and Eq. 1 usually written as

$$BE_i = E_i^{N-1}(\text{SCF}) - E^N(\text{SCF}) \quad (2)$$

where the subindex i in BE_i indicates the ionized core whereas $E^N(\text{SCF})$ and $E_i^{N-1}(\text{SCF})$ are the variationally optimized energy for the initial system with N electrons and the final systems with $(N-1)$ electrons and the corresponding i core hole. It is customary to decompose BE_i into initial and final states^{9,10} This, however, will not be considered here since the main goal is to assess the accuracy on the BEs rather than to analyze the initial and final state contributions.

3. Molecular Data Set and Computational Details

Calculations have been performed on a series of main group molecules containing at least one of the following main group elements: B, C, N, O, and F. Δ BEs are, for each core level, computed with respect to a given reference molecule: diborane (B_2H_6), methane (CH_4), ammonia (NH_3), water (H_2O), and fluoromethane (CH_3F) for $\text{B} \rightarrow \text{F}$, respectively.

The chosen molecular data set is listed in Appendix A and it is fully described in Table S1 of the Supplementary Information; overall it includes 68 molecules and 185 core levels BEs whose experimental values, obtained from XPS experiments, are available.²⁷⁻³⁰ These molecules were carefully chosen featuring also different organic functional groups. Thus, the set ranges from very simple homonuclear diatomic molecules such as O_2 and F_2 , to very complex ones such as $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$. A criterion was set to select molecules so that the different possible neighboring chemical environments and chemical functional groups are represented, allowing for obtaining meaningful general information about the proper physicochemical description of core electrons by the different computational methods explored.

The calculations have been carried out using a large fully-uncontracted basis set near the HF limit, ensuring an accurate and well-defined description of both neutral and ionized states. Specifically for $\text{B} \rightarrow \text{F}$, an uncontracted Partridge ($14s, 9p$) set augmented by a d function taken from the polarized Valence Triple Zeta ($pVTZ$) set was used. For H atoms we used an uncontracted basis set ($5s$) taken from the VTZ basis set augmented with a p function.³¹

In the present work we use the HF method as reference since it has been widely used to interpret and predict BEs,^{9,10,32-34} even if it is not well suited for periodic calculation involving metals. From the different DFT methods available we have

selected PBE as a prototype of the GGA family and the TPSS from the meta-GGA since both functionals are best suited to describe metal substrates,^{19,20} and, as commented, TPSS also constitutes an improvement of PBE for the thermochemistry of main group element containing molecules. Here, we explore the performance of TPSS in predicting BEs and Δ BEs of simple molecules representative of the systems one may encounter in surface science and heterogeneous catalysis.

For each of the three methods explored, the equilibrium geometry of each molecule is optimized for the neutral molecule. In a recent work,¹⁵ it has been demonstrated that there is no significant differences in predicting BEs and Δ BEs as a function of the optimized geometry, *i.e.* a common geometry obtained at a given level can be safely used, frozen, at other levels, although here we decided to self-consistently optimize the structures. Using a common geometry, preferably experimental geometry, may be useful when aiming at analyzing the BEs and Δ BEs of a given molecule using different methods. However, using the optimized structures is preferred here since by appropriate frequency analyses one can ensure that they represent a minimum in the corresponding potential energy hypersurface, as this has been carried out for all cases. Note also that Δ SCF calculations aimed to obtain BEs and Δ BEs values are carried out at the geometry of the neutral molecule, *i.e.* vertical transitions, which is a reasonable choice given the time scale of core level ionization in the XPS experiments. All calculation have been performed with the GAMESS program.^{35,36} For the core hole state the occupied orbitals are selected using an overlap criterion instead of the usual Aufbau approach. All calculations have been carried out in a spin restricted fashion and are non-relativistic.

However relativistic effects are different for different core levels and increase with the atomic number of the ionized atom. Therefore to discuss the accuracy of the different methods in predicting BEs it is convenient to have a reliable estimate of the contribution of the relativistic effects. To this end, results from relativistic and non-relativistic calculations for the B→F isolated atoms at the HF level of theory provided by Bagus³⁷ have been used. These relativistic calculations were carried out with the DIRAC program³⁸ and the non-relativistic calculations were carried out with the CLIPS code.³⁹ The wave functions were based on the average of configurations and do not take into account the multiplet splittings for these open shell atoms.⁴⁰ We compared fully relativistic four-component Dirac HF wave functions and energies with non-relativistic HF wavefunctions and energies for the B→F isolated atoms. The basis sets used for these calculations were the same as for the other calculations. It is worth pointing out that previous works,^{14,15} validated the GAMESS results for the core hole states by comparing to results obtained with CLIPS.

4. Results and Discussion

Let us first analyze the absolute BE(Δ SCF) results, the Δ BE(Δ SCF) values, and their respective dispersion with respect the experimental values for the entire molecular dataset, but itemized according to different heteroatoms. The calculated BE(Δ SCF) values for the B→F atoms are represented in Figure 1. We start discussing the PBE results as shown in Figure 1. Generally speaking the PBE BE(Δ SCF) results, regardless of the studied element, are lower than those calculated with HF or TPSS, which in turn are closer to the experimental values. The statistical treatment of each B→F core level BEs is also given in Table 1 by calculating the Mean Error (*ME*), Mean Absolute Error (*MAE*), and the Mean Absolute Percentage Error (*MAPE*). Note that ME and MAE for

PBE are mostly the same value with the only difference of sign; hence, PBE systematically underestimates BEs. Note aside that ME and MAE increase throughout the B→F series, a trend which is explained below. Nevertheless, mind that MAPE, even though PBE leads to the worst absolute BE(Δ SCF) values, is of 0.38% only for the worst scenario. Thus, relying on MAPE for the absolute value of BEs may be misleading simply because BEs are very large. On the other hand, ME and MAE clearly indicate that, compared to HF and TPSS, PBE prediction of core level BE(Δ SCF) values is less accurate even if, in absolute terms, it presents a very small error with respect to experimental values.

We focus now on the accuracy of HF and TPSS calculated BE(Δ SCF) values. In the N, O, and F cases the HF and TPSS results are, according to Table 1, similar, but HF values tend to be smaller than experiment whereas TPSS are often larger. The trend in HF is, as expected, since electron correlation effects, not included in HF, are larger for the neutral molecule thus leading to too small BEs. Nevertheless, the calculated core level BEs are most often consistently lower than the experimental BEs as seen in Figure 1, and thus behave similar to PBE. Note by passing that for O there are outliers, in particular, O₂ and H₂O₂, whose disagreement is translated to the Δ BEs, see below, although one has to keep in mind that we deal here with average behaviors, instead of particular agreements. When the BE(Δ SCF) values are analyzed for B- and C-containing molecules, the ME and MAE values start to show a higher disagreement with experiment; the error associated is not systematic, and this is reflected in Figure 1 by values above and below the experimental ones. Nevertheless, BEs for the 1s core of these molecules get really close to the experimental ones, note that the difference is only 0.3 eV for both HF and TPSS, close to the XPS experimental precision of \sim 0.1 eV.

TPSS is slightly better than HF by ~ 0.04 eV. This better adequacy increases for N \rightarrow F to improvements up to 0.31 eV.

From another point of view one can analyze BEs of molecules in terms of their respective shifts relative to a reference molecule. Figure 2 represents the $\Delta\text{BE}(\Delta\text{SCF})$ values with respect to the experimental shifts, $\Delta\text{BE}(\text{Exp.})$, for each element using the reference molecules indicated above. The most evident difference, in comparison to $\text{BE}(\Delta\text{SCF})$ values in Figure 1, is that there is no significant variations of the shifts with respect to the used method. As expected, the systematic errors cancel each other. To further analyze the core level ΔBEs the statistical analysis is reported in Table 2. The ME results at HF and TPSS levels of theory are, in general terms, negative, with the caveat for N_{1s} , which appears to show an agreement within chemical accuracy. Curiously, this happens for all ME PBE values with the caveat of F_{1s} results. Notwithstanding that, the MAE values do not follow the same trend above described. For the three studied methods the MAEs are similar one to each other as it is shown in Table 2. For the $\Delta\text{BE}(\Delta\text{SCF})$ values, MAPE is not reported since here the values are much smaller and variations of a few tenths of an eV translated into physically meaningless MAPE values. The full absolute core level $\text{BE}(\Delta\text{SCF})$ and $\Delta\text{BE}(\Delta\text{SCF})$ data are reported in Table S1 in the Supporting Information.

So far, the discussion concerned non-relativistic calculations. We indeed considered the influence of relativistic effect on the $1s$ BEs on the studied elements. Relativistic (*Rel.*) and non-relativistic (*Non-Rel.*) calculations have been carried out for the B \rightarrow F atoms, and the relativistic contributions and the comparison with the non-relativistic ones are shown in Table 3. The relativistic change in the final state, including the relaxation of the electrons with a core-hole, *Diff.*, is defined as:

$$Diff = BE(\Delta SCF, Rel) - BE(\Delta SCF, Non-Rel) \quad (3)$$

It has been reported¹⁵ that the relativistic changes on the initial and final states are very close with each other, which means that the relativistic changes are dominant, already at the initial state. Since we want to establish the relativistic contribution to the absolute core level BEs, the changes were studied for the $BE(\Delta SCF)$ values. The Diff. values in Table 3 show that the relativistic $1s$ core BEs are larger than the non-relativistic values, although the relativistic effects lead to a very small increase in the core level BEs for these light atoms as expected; from 0.06 eV for B to 0.75 eV for F, thus increasing along the B→F series, as expected.

When we analyze the $BE(\Delta SCF)$ and the $\Delta BE(\Delta SCF)$ for the whole data set, the above obtained excellent agreement is maintained, *i.e.* mixing of B→F results does not disrupt the statistics. On the contrary, the overall performance is enhanced. The statistical analysis values for the overall calculations, with or without including the relativistic changes, are reported in Table 4. The absolute non-relativistic BEs and their ΔBE s are shown in Figures 3 and 4, respectively. Inspecting the data on Table 4, it is seen that for the absolute non-relativistic BEs for the entire set, the PBE results are worse than the HF or TPSS with ME and MAE values of ~ 1 eV. The HF and TPSS BEs errors are similar and within 0.3-0.4 eV from experimental values.

Note that when relativistic contributions are included, the BEs values approach the experimental ones, and so, discrepancies owed, in part, due to such an approximation. However, even including relativistic effects, PBE results are still worse in comparison to the other two methods, with ME and MAE values of ~ 0.8 eV. Still HF and TPSS statistics are similar, and ME and MAE values drop to 0.2-0.3 eV, very close to the XPS chemical accuracy. Relativistic effects explain in part the disagreements

with respect the experimental values and the fact that, for a given core, this effect is constant implies that both HF and TPSS are excellent methods in predicting BEs with PBE performing slightly worse.

Let us now analyze the Δ BE values for the different $1s$ cores. As it is shown in Table 4 for both non-relativistic and relativistic results, the agreement between methods and with experimental values is really excellent and better than for the absolute BE(Δ SCF) values, leading to ME results from ~ 0 to -0.2 eV and MAE values in between 0.2 - 0.3 eV. Surprisingly, when using the full calculation set, the PBE method leads to Δ BE balanced results very close to HF and TPSS. Thus, the three methods perform excellent and are, *a priori*, adequate to assign species based on Δ BEs, as done previously for compounds on solid surfaces.⁴¹⁻⁴³

Figure 3 displays BE(Δ SCF) results *versus* experimental BEs, a perfect linear fitting is clearly seen. The linear trend is also observed when comparing calculated *versus* experimental Δ BE values. In Table 5 a summary of the offsets respect to the ideal cases, with and without the relativistic contributions, is reported. The rest of parameters of the regression treatment, regression coefficients, slopes, and intercepts are included in Table S2 in the Supporting Information. However, note that regression coefficients of the full dataset are above 0.98 . Let us now consider the Δ BE for the different cores, the intercepts are near the ideal cut at 0 eV, with a slight dispersion, depending on the element analyzed and the method used, yet in average is ~ 0.02 eV for PBE and HF, and ~ 0.27 eV for TPSS. Considering the mean variation between the experimental and the calculated values for the full set of data leads to offsets for the three different levels of calculation, small, with a positive difference ~ 0.3 eV at HF, and ~ -0.3 eV at TPSS and PBE, see Table 5. This highlights once more that these three

methods provide reliable estimates of the core level shifts, with very small differences with respect to the experimental values. Nevertheless, one should keep in mind that HF overestimates Δ BEs, whereas DFT underestimates them. Regarding the absolute BE(Δ SCF) values, the intercepts are much higher than for Δ BEs simply because a small deviation on the slope is magnified by the large range of energies considered, see Figure 3.

One can better determine the ideal deviation by further analyzing the offsets. Here we gained the offsets for the non-relativistic calculations, and offsets taking into account the relativistic contributions. First, we analyze the non-relativistic offsets to give a brief idea of the cases studied and next, the study with the relativistic effects will be also discussed. For the full set, the overall obtained offsets; including or not the relativistic corrections, are always below the experiment. The non-relativistic offset results itemized for each B \rightarrow F atoms studied, generally increase following the series, yet the tendency along methods is kept. Results from PBE, as previously shown, lead to results with the largest deviation respect to the linearity, from -0.7 to -1.8 eV, with a global offset of \sim -1.2 eV. The results from HF and TPSS are akin to each other or, in many cases, better for TPSS. The offsets range from -0.02 to -0.8 eV, representing the closest or least deviated trend compared to ideality. When taking into account the full set, the offset is \sim -0.4 eV. Including the relativistic contribution to the BEs improves the already excellent agreement with experiment. For HF and TPSS, the offsets become now -0.11 eV and -0.05 eV, respectively, well within XPS chemical accuracy.

In light of the above presented discussion, the obtained results for the three explored methods, with and without relativistic corrections, are very good when computing Δ BEs of main group organic molecules, and HF, and specially the TPSS xc

are excellent in predicting absolute core level BEs, when relativistic effect are considered. Thus, TPSS poses itself as an convenient and accurate method for the study of core level BEs of adsorbates of main group elements on metallic surfaces which, given its suitability in describing bulk transition metals and the thermochemistry of organic molecules, appears to be an excellent choice to study this type of systems.

5. Conclusions

Here we have explored the performance of HF, PBE and TPSS methods in predicting 1s core level BEs of a set of 68 molecules (185 core levels explored in total) containing a wide variety of functional groups and chemical environments for main group elements B→F. The obtained results using Δ SCF methodology have been compared to reported experimental references. This has been carried out in a non-relativistic fashion, yet the relativistic effects have been explicitly considered on isolated atoms, and, since are known to be independent of the particular chemical environment, added *a posteriori* on the obtained estimates.

The analysis yields that computed absolute core level BEs are, overall, and regardless of the method, in very good agreement with the reported experimental values. Nevertheless, it is important to highlight that TPSS values are slightly better than those predicted from HF and these two clearly better than PBE. The BEs values have also been analyzed in terms of shifts, Δ BEs, from selected references. As long as Δ BEs are concerned, the three methods yield very similar and excellent results, with mean absolute deviations of ~ 0.25 eV.

When relativistic effects are included BE(Δ SCF) deviations drop and estimations get much closer to the experimental values. Linear relationships have been found between experimental and estimated values, obtaining, for any method, and any set or

subset of data, an offset with respect to ideal linearity. Correcting the values by including the relativistic effects leads to offsets of 0.11 and 0.05 eV for HF and TPSS, respectively. Both, HF and TPSS methods slight underestimate the experimental BEs but within the accuracy of the XPS measurement. Thus, TPSS is posed as an excellent choice for the characterization, by XPS, of molecules on metal solid substrates, given its suitability in describing metal substrates bonds *and* atomic and/or molecular orbitals.

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